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(54) LUBRICATING OIL COMPOSITION

(57) There is provided a lubricating oil composition which is excellent in resistance to oxidation and which can maintain the effect of reducing friction caused in engines without undergoing deterioration by being adversely affected by nitrogen oxides gas.

The lubricating oil composition comprises a lubricating base oil and the following components: an oxymolybdenum sulfide dithiocarbamate having a specific structure, a zinc dialkyl dithiophosphate, a sulfur compound, a metallic detergent and a boron-containing compound, wherein the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate is from 200 to 2,000 ppm of the total weight of the composition, the amount of phosphorus derived from the zinc dialkyl dithiophosphate is from 0.02 to 0.15% by weight of the total weight of the composition, the amount of sulfur derived from the sulfur compound is from 0.02 to 0.30% by weight of the total weight of the composition,

the amount of the metallic detergent is from 1 to 10% by weight of the total weight of the composition, and the amount of boron derived from the boron-containing compound is from 0.005 to 0.06% by weight of the total weight of the composition.

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Description

Field of the Invention

5 The present invention relates to a novel lubricating oil composition. More specifically, the present invention relates to a lubricating oil composition useful as a lubricating oil for internal-combustion engines, automatic transmissions, dampers and power steering, particularly useful as a lubricating oil for internal-combustion engines, which composition has excellent antiwear properties and friction reducing properties and can maintain the friction-reducing properties for a prolonged period of time without undergoing deterioration even in the air containing nitrogen oxides gas.

10 Lubricating oils are used for internal-combustion engines, and for driving units and gears such as automatic transmissions, dampers and power steering in order to ensure smooth operation thereof. In particular, lubricating oils for internal-combustion engines not only lubricate various sliding portions such as a contacting surface between a piston ring and a cylinder liner, a bearing for a crank shaft or a connecting rod, and a valve-operating mechanism including a cam and a valve lift, but also cool the inside of the engines, clean and disperse combustion products, and prevent the rusting and corrosion of the engines.

15 Thus, lubricating oils for internal-combustion engines have been required to have a great variety of properties. Moreover, higher-performance lubricating oils are now required due to the recent trend high-performance in internal-combustion engines such as the trend toward lower rates of fuel consumption, the trend toward high-output and the trend toward severer operating conditions therein. On the other hand, combustion gas generated in an internal-combustion engine partially leaks between a piston and cylinder therein, and comes into a crank case as blowby gas. Such combustion gas contains nitrogen oxides gas in a considerably high concentration. The nitrogen oxides gas deteriorates, along with oxygen contained in the blowby gas, the lubricating oil used for the internal-combustion engine. Due to the recent trend toward high-performance in internal-combustion engines, there is such a tendency that the concentration of nitrogen oxides gas which comes into a crank case is increased. In order to make lubricating oils for internal-combustion engines meet the above-described requirements and undergo no deterioration even in the air containing nitrogen oxides gas, various additives such as antiwear agents, metallic detergents, nonash dispersants and antioxidants are added to them, accordingly.

20 It is particularly important as an essential function of lubricating oils for internal-combustion engines that the lubricating oils can ensure the smooth operation of the engines under every condition to prevent the wear and seizure of the engines. The lubricated parts of the engines are, for the most part, under the fluid lubrication condition. However, a valve-operating system, and the top and bottom dead centers of a piston tend to come under the boundary lubrication condition. Antiwear properties shown under the boundary lubrication condition are generally imparted to lubricating oils by the addition of zinc dithiophosphate.

25 Energy loss at the frictional parts of internal-combustion engines which are lubricated by lubricating oils is so great that a friction modifier is added to the lubricating oils in order to reduce the friction loss and to decrease the rate of fuel consumption. For example, an organic molybdenum compound, a fatty ester, or an alkylamine is usually used as the friction modifier.

30 Under such circumstances, we made earnest studies. As a result, it was found that although such a friction modifier is effective at the outset of its use, it loses its effects when undergoes oxidative degradation by oxygen contained in the air, in particular, the effects are drastically impaired in the presence of nitrogen oxides gas. An object of the present invention is therefore to provide a lubricating oil composition which can maintain, for a long period of time, the effect of reducing friction caused in engines without being adversely affected by nitrogen oxides gas.

35 We have made earnest studies in order to develop a lubricating oil composition having the above-described advantageous properties, and, as a result, found that the above object of the invention can be attained by a composition which is obtained by blending, with a lubricating base oil, an oxymolybdenum sulfide dithiocarbamate having a specific alkyl group, a zinc dialkyl dithiophosphate having a specific alkyl group, a specific sulfur compound, a specific metallic detergent and a boron-containing compound, each in a predetermined amount. The present invention has been accomplished on the basis of this finding.

40 Namely, the present invention provides (1) a lubricating oil composition comprising a lubricating base oil and the following components.

(A) an oxymolybdenum sulfide dithiocarbamate having an alkyl group containing 8 to 18 carbon atoms,

45 (B) a zinc dialkyl dithiophosphate having a primary alkyl group containing 1 to 18 carbon atoms,

50 (C) one or more sulfur compounds selected from the group consisting of zinc dialkyl dithiocarbamates, copper dialkyl dithiocarbamates or nickel dialkyl dithiocarbamates having an alkyl group containing 2 to 18 carbon atoms, tetraalkylthiuram disulfides having an alkyl group containing 2 to 18 carbon atoms, disulfides having an alkyl group

containing 2 to 18 carbon atoms, disulfides having an aryl, alkyl aryl or aryl alkyl group containing 6 to 18 carbon atoms, thiadiazole compounds having a substituent which contains 3 to 24 carbon atoms and sulfur, olefin sulfides, sulfides of fish oil and sulfides of whale oil,

(D) one or more metallic detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate and calcium phenate, and

(E) a boron-containing compound,

characterized in that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate is from 200 to 2,000 ppm (weight basis) of the total weight of the composition, the amount of phosphorus derived from the zinc dialkyl dithiophosphate is from 0.02 to 0.15% by weight of the total weight of the composition, the amount of sulfur derived from the sulfur compound(s) is from 0.02 to 0.30% by weight of the total weight of the composition, the amount of the metallic detergent(s) is from 1 to 10% by weight of the total weight of the composition, and the amount of boron derived from the boron-containing compound is from 0.005 to 0.06% by weight of the total weight of the composition.

Further, there can be mentioned the following lubricating oil compositions as preferred embodiments of the present invention:

(2) a lubricating oil composition as set forth in the above item (1), wherein (A) the oxymolybdenum sulfide dithiocarbamate has an alkyl group containing 8 to 13 carbon atoms, (B) the zinc dialkyl dithiophosphate has primary alkyl group containing 3 to 12 carbon atoms, and (C) the boron-containing compound is boron-containing succinimide; and

(3) a lubricating oil composition as set forth in the above item (1) or (2), wherein the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate is from 300 to 800 ppm (weight basis) of the total weight of the composition, the amount of phosphorus derived from the zinc dialkyl dithiophosphate is from 0.04 to 0.12% by weight of the total weight of the composition, and the amount of boron derived from the boron-containing compound is from 0.01 to 0.04% by weight of the total weight of the composition.

The present invention will now be explained in detail.

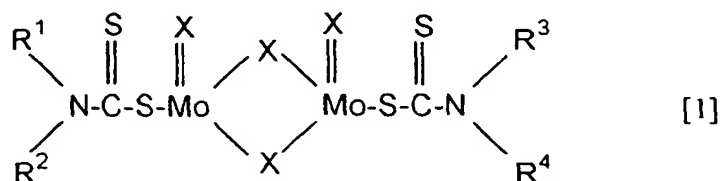
There is no particular limitation on the lubricating base oil for use in the lubricating oil composition of the present invention, and any base oil, such as any of mineral oils and synthetic oils, which is commonly used for the conventional lubricating oils can be used.

Examples of the mineral oils include raffinates obtained by subjecting raw materials for lubricating oils to solvent refining which is effected by using an aromatic extraction solvent such as phenol or furfural, hydrogenated oils obtained by subjecting raw materials for lubricating oils to hydrogenation treatment which is carried out by using a hydrogenation catalyst such as cobalt or molybdenum supported on a silica-alumina carrier, and lubricating oil fractions obtained by the isomerization of waxes, such as 60 neutral oil, 100 neutral oil, 150 neutral oil, 300 neutral oil, 500 neutral oil and bright stocks.

On the other hand, examples of the synthetic oils include poly(α -olefin) oligomers, polybutene, alkylbenzene, polyol esters, polyglycol esters, esters of dibasic acids, phosphoric esters and silicone oil. These base oils can be used either singly or in combination of two or more. Further, a mixture of mineral oil and synthetic oil can also be used in the present invention.

Those oils whose viscosities at 100°C are in the range of 3 to 20 mm²/s are preferable as the base oils for use in the lubricating oil composition of the present invention. Of these, hydrocracked oils and wax-isomerized oils which contain 3% by weight or less of aromatics, 50 ppm or less of sulfur and 50 ppm or less of nitrogen are particularly preferred.

A compound represented by the following general formula [1] is used as the oxymolybdenum sulfide dithiocarbamate to be incorporated into the lubricating oil composition of the present invention:



wherein R¹, R², R³ and R⁴, which may be the same or different, each represents an alkyl group having 8 to 18 carbon atoms, and X is sulfur or oxygen.

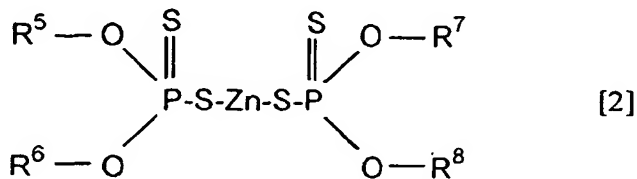
The alkyl group having 8 to 18 carbon atoms, represented by R¹, R², R³ or R⁴ in the general formula [1] can be either linear or branched. In the lubricating oil composition of the present invention, it is particularly preferable that the alkyl group represented by R¹, R², R³ or R⁴ has 8 to 13 carbon atoms.

Specific examples of the alkyl group represented by R¹, R², R³ or R⁴ include octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups.

In the lubricating oil composition of the present invention, either one or two or more oxymolybdenum sulfide dithiocarbamates can be used. Further, the oxymolybdenum sulfide dithiocarbamate is incorporated into the composition so that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate can be from 200 to 2,000 ppm (weight basis), preferably from 300 to 800 ppm (weight basis) of the total weight of the composition. When the oxymolybdenum sulfide dithiocarbamate is incorporated into the composition in such an amount that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate is less than 200 ppm (weight basis) of the total weight of the composition, the effect of improving frictional properties (friction-reducing properties) cannot be fully obtained.

On the other hand, when the oxymolybdenum sulfide dithiocarbamate is incorporated into the composition in such an amount that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate is in excess of 2,000 ppm (weight basis) of the total weight of the composition, the effect cannot be enhanced in proportion to such an increased amount of the oxymolybdenum sulfide dithiocarbamate, and sludges or the like tend to be formed.

A compound represented by the following general formula [2] is used as the zinc dialkyl dithiophosphate to be incorporated into the lubricating oil composition of the present invention:

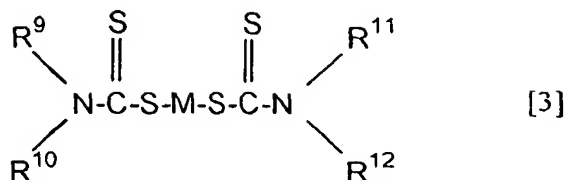


wherein R⁵, R⁶, R⁷ and R⁸, which may be the same or different, represent a primary alkyl group having 1 to 18 carbon atoms.

The primary alkyl group represented by R⁵, R⁶, R⁷ or R⁸ in the general formula [2] can be either linear or branched. Examples of such a primary alkyl group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups. It is particularly preferable to use, in the lubricating oil composition of the present invention, a zinc dialkyl dithiophosphate having a primary alkyl group containing 3 to 12 carbon atoms.

In the lubricating oil composition of the present invention, the zinc dialkyl dithiophosphate is incorporated so that the amount of phosphorus derived from the zinc dialkyl dithiophosphate can be from 0.02 to 0.15% by weight, preferably from 0.04 to 0.12% by weight of the total weight of the composition. When the zinc dialkyl dithiophosphate is incorporated into the composition in such an amount that the amount of phosphorus derived from the zinc dialkyl dithiophosphate is less than 0.02% by weight of the total weight of the composition, the resulting composition is poor in antiwear properties, and, in addition, cannot show a satisfactorily low coefficient of friction under the operating conditions of high oil temperatures and low rotational speeds. On the other hand, when the zinc dialkyl dithiophosphate is incorporated into the composition in such an amount that the amount of phosphorus derived from the zinc dialkyl dithiophosphate is in excess of 0.15% by weight of the total weight of the composition, the effect cannot be enhanced in proportion to such an increased amount of the zinc dialkyl dithiophosphate.

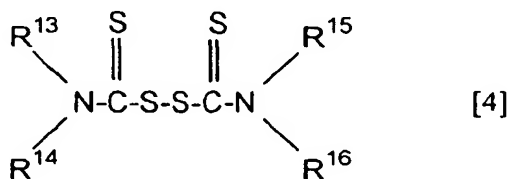
A compound represented by the following general formula [3] is used as the dialkyl dithiocarbamate to be incorporated into the lubricating oil composition of the present invention:



wherein M is zinc, copper or nickel, and R⁹, R¹⁰, R¹¹ and R¹², which may be the same or different, represent an alkyl group having 2 to 18 carbon atoms.

The alkyl group having 2 to 18 carbon atoms, represented by R⁹, R¹⁰, R¹¹ or R¹² in the general formula [3] can be either linear or branched. Examples of such an alkyl group include ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups.

A compound represented by the following general formula [4] is used as the tetraalkylthiuram disulfide to be incorporated into the lubricating oil composition of the present invention:



wherein R¹³, R¹⁴, R¹⁵ and R¹⁶, which may be the same or different, represent an alkyl group having 2 to 18 carbon atoms.

The alkyl group having 2 to 18 carbon atoms, represented by R¹³, R¹⁴, R¹⁵ or R¹⁶ in the general formula [4] can be either linear or branched. Examples of such an alkyl group include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups.

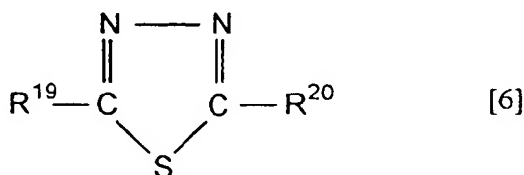
A compound represented by the following general formula [5] is used as the disulfide to be incorporated into the lubricating oil composition of the present invention:



wherein R¹⁷ and R¹⁸, which may be the same or different, represent an alkyl group having 2 to 18 carbon atoms, or an aryl group.

The alkyl group having 2 to 18 carbon atoms, represented by R¹⁷ or R¹⁸ in the general formula [5] can be either linear or branched. Examples of such an alkyl group include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups. Further, examples of the aryl, alkyl aryl or aryl alkyl group having 6 to 18 carbon atoms, represented by R¹⁷ or R¹⁸ include phenyl, benzyl, phenethyl, methylbenzyl and diphenylmethyl groups.

A compound represented by the following general formula [6] is used as the thiadiazole compound having a substituent which contains sulfur, to be incorporated into the lubricating oil composition of the present invention:



wherein R¹⁹ and R²⁰, which may be the same or different, represent a monovalent group containing 3 to 24 carbon atoms and one or more sulfur atoms.

Examples of the monovalent group containing 3 to 24 carbon atoms and one or more sulfur atoms, represented by R^{19} or R^{20} in the general formula [6] include 5-thianonyl, 2,5-dithiahexyl, 3,4-dithiahexyl, 4,5-dithiahexyl, 3,4,5-trithiaheptyl, 3,4,5,6-tetrathiaoctyl, 5-thia-2-heptenyl, 4-thiacyclohexyl, 1,4-dithianaphthyl, 5-(methylthio)octyl, 4-(ethylthio)-2-pentenyl, 4-(methylthio)cyclohexyl, 4-mercaptophenyl, 4-(methylthio)phenyl and 4-(hexylthio)benzyl groups. Of these, particularly preferable groups are those in which 2 to 4 sulfur atoms are sequentially combined in the chain, for instance, 3,4-dithiahexyl group represented by the formula [7], 4,5-dithiahexyl group represented by the formula [8], 3,4,5-trithiaheptyl group represented by the formula [9], and 3,4,5,6-tetrathiaoctyl group represented by the formula [10]:



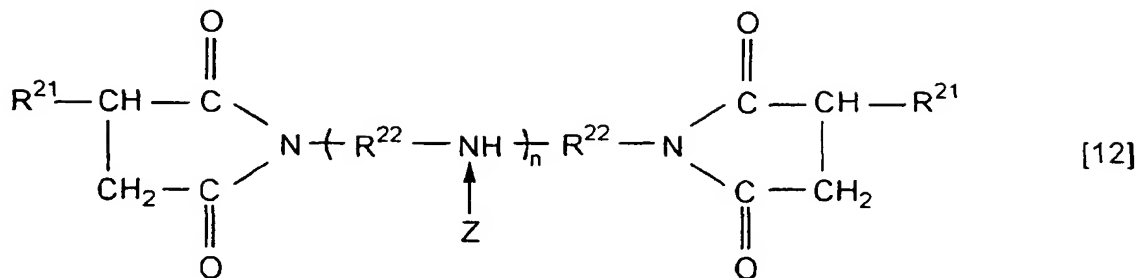
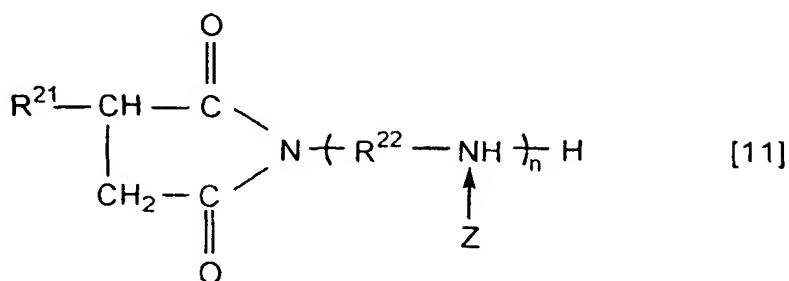
The olefin sulfide to be incorporated into the lubricating oil composition of the present invention is an olefin sulfide containing 25 to 40% by weight of sulfur, obtained by sulfurizing a polymer of isobutylene or the like. The sulfide of fish oil or whale to be incorporated into the lubricating oil composition of the present invention is one obtained by likewise sulfurizing fish oil or whale oil.

In the lubricating oil composition of the present invention, the dialkyl dithiocarbamates represented by the general formula [3], the tetraalkylthiuram disulfides represented by the general formula [4], the disulfides represented by the general formula [5], the thiadiazole compounds represented by the general formula [6], the olefin sulfides, the sulfides of fish oil and the sulfides of whale oil can be used either singly or in combination of two or more. These sulfur compounds are incorporated into the composition so that the amount of sulfur derived from the sulfur compounds can be from 0.02 to 0.30% by weight of the total weight of the composition. When the sulfur compounds are incorporated into the composition in such an amount that the amount of sulfur derived from the sulfur compounds is less than 0.02% by weight of the total weight of the composition, the resulting composition cannot fully maintain the friction-reducing properties for a long period of time. On the other hand, when the sulfur compounds are incorporated into the composition in such an amount that the amount of sulfur derived from the sulfur compounds is in excess of 0.30% by weight of the total weight of the composition, the effect cannot be enhanced in proportion to such an increased amount of the sulfur compounds.

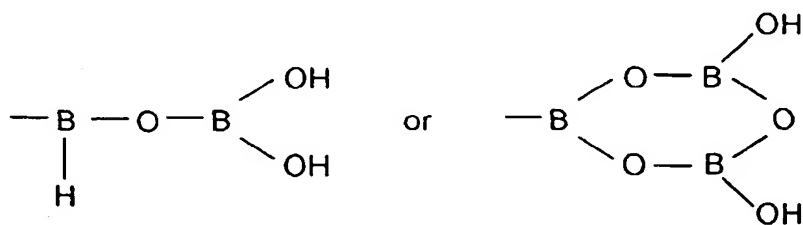
One, or two or more metallic detergents selected from the group consisting of calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium phosphate and calcium phenate are incorporated into the lubricating oil composition of the present invention. These metallic detergents are incorporated into the composition in an amount of 1 to 10% by weight of the total weight of the composition. When the amount of the metallic detergents is less than 1% by weight of the total weight of the composition, cleaning effect cannot be fully obtained. On the other hand, when the amount of the metallic detergents is in excess of 10% by weight of the total weight of the composition, the effect cannot be enhanced in proportion to such an increased amount of the metallic detergents, and, instead, the ash content is increased.

In the lubricating oil composition of the present invention, the total base number of the composition is adjusted to preferably 3 to 10, more preferably 4 to 7. The total base number of the composition can be determined in accordance with JIS K2501. The total base number of the composition can be suitably adjusted by selecting metallic detergents having proper base numbers.

Specific examples of the boron-containing compound for use in the lubricating oil composition of the present invention include boron-containing succinimides and boron-containing succinates. Examples of the boron-containing succinimides include those compounds which are represented by the following general formula [11] or [12]:

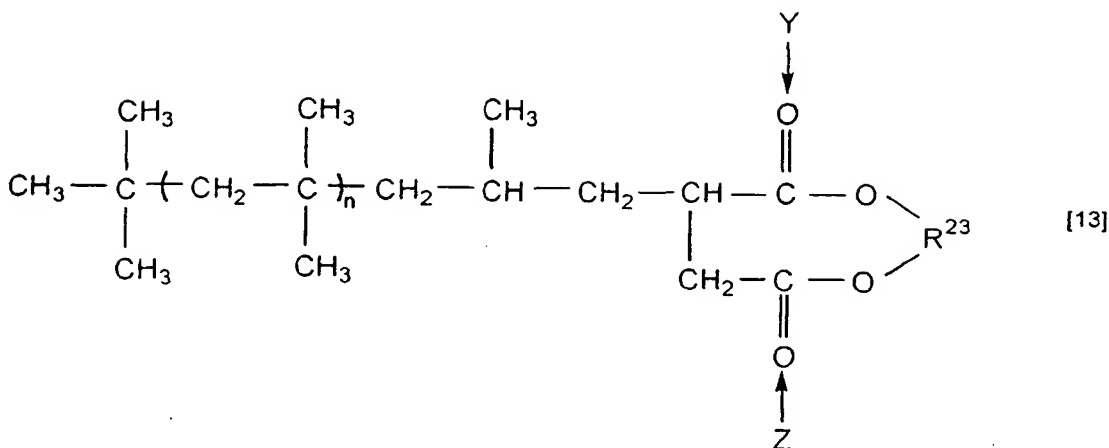


wherein R^{21} is a hydrocarbon group having 1 to 50 carbon atoms, R^{22} is an alkylene group having 2 to 5 carbon atoms, n is a number of 1 to 10; two R^{21} 's in the compounds of the general formula [12] may be the same or different and R^{22} 's in the number of " n " in the general formula [11] or of " $n+1$ " in the general formula [12] may be the same or different; and Z is a boron-containing substituent having such as the following structure:



Specifically, "ECA 5025" (manufactured by Exxon Chemical Co. Ltd.), "LUBRIZOL 935" (manufactured by THE LUBRIZOL CORP.) and the like can be enumerated.

Further, examples of the boron-containing succinates include those compounds which are represented by the following general formula [13]:



wherein n is a number of 1 to 20; R²³ is a linear or branched hydrocarbon group having 2 to 18 carbon atoms, which can contain therein an aromatic or double bond; and Y and Z are boron-containing substituents, at least one of them being co-ordinated to the succinate by co-ordination bond.

Specifically, "LUBRIZOL 936" (manufactured by THE LUBRIZOL CORP.) and the like can be enumerated.

Of the boron-containing compounds, the boron-containing succinimides are preferred. Further, the combination use of the boron-containing succinate and a succinimide which will be described later is also a useful means. The boron-containing compound is incorporated into the composition in such an amount that boron derived from the boron-containing compound can be from 0.005 to 0.06% by weight, preferably from 0.01 to 0.04% by weight of the total weight of the composition. When the boron-containing compound is incorporated into the composition in such an amount that the amount of boron derived from the boron-containing compound is less than 0.005% by weight of the total weight of the composition, the resulting composition cannot have sufficiently improved frictional properties (friction-reducing properties). On the other hand, when the boron-containing compound is incorporated into the composition in such an amount that the amount of boron derived from the boron-containing compound is in excess of 0.06% by weight of the total weight of the composition, the effect cannot be enhanced in proportion to such an increased amount of the boron-containing compound.

Various additives which are usually incorporated into the conventional lubricating oils, such as other friction modifiers, other metallic detergents, other anti-wear agents, other non-ash dispersants, anti-oxidants, viscosity index improvers, pour point depressants, anti-foaming agents, rust preventives and corrosion inhibitors, can be added, if necessary, to the lubricating oil composition of the present invention within such a limit that they do not disturb the attainment of the object of the present invention.

Examples of other friction modifiers include partially-esterified polyhydric alcohols, amines, amides and sulfate esters.

Examples of other metallic detergents include barium sulfonate and barium phenate. In general, they are added to the composition in an amount of 0.1 to 5% by weight.

Examples of other anti-wear agents include metallic salts of thiophosphoric acid, sulfur compounds, phosphoric esters and phosphorous esters. In general, they are added to the composition in an amount of 0.05 to 5.0% by weight.

Examples of other non-ash dispersants include those of succinimide type, succinamide type, benzylamine type and ester type. In general, they are added to the composition in an amount of 0.5 to 7% by weight.

Examples of the anti-oxidants include amine anti-oxidants such as alkylated diphenylamine, phenyl - α - naphthylamine and alkylated α - naphthylamine, and phenolic anti-oxidants such as 2,6-di-*t*-butyl-4-methylphenol and 4,4'-methylene-bis(2,6-di-*t*-butylphenol). In general, they are added to the composition in an amount of 0.05 to 4% by weight.

Examples of the viscosity index improvers include those of polymethacrylate type, polyisobutylene type, ethylene-propylene co-polymer type and styrene-butadiene hydrogenated co-polymer type. In general, they are added to the composition in an amount of 0.5 to 35% by weight.

Examples of the pour point depressants include polyalkyl-methacrylate, chlorinated paraffin-naphthalene condensation products and alkylated polystyrene.

Examples of the anti-foaming agents include dimethyl polysiloxane and polyacrylic acid.

Examples of the rust preventives include fatty acids, partially-esterified alkylenyl succinates, fatty acid soaps, alkyl sulfonates, fatty polyhydric alcohol esters, fatty amines, paraffin oxides and alkyl polyoxyethylene ethers.

Examples of the corrosion inhibitors include benzotriazole and benzoimidazole.

The present invention will now be explained more specifically by referring to the following Examples. However, the present invention is not limited by these examples in any way.

The co-efficients of friction of the lubricating oil compositions were determined by a reciprocating sliding friction tester [SRV Friction Tester] under the conditions of a frequency of 50 Hz, an amplitude of 3 mm, a load of 25N, a temperature of 80°C and a test time of 25 minutes.

Further, the test for oxidation by the air containing nitrogen oxides gas was carried out by exposing, for 8 hours, 150 ml of a sample oil to the air of 130°C, containing 1 volume % of nitrogen oxides (NOx), flown at a rate of 2 litres/hour.

Examples 1 to 10 and Comparative Examples 1 and 2

Lubricating oil compositions of Examples 1 to 10 are those which contain (A) an oxymolybdenum sulfide dithiocarbamate, (B) a zinc dialkyl dithiophosphate, (C) zinc diamyl dithiocarbamate, copper dibutyl dithiocarbamate, tetrabutylthiuram disulfide, dibenzyl disulfide or di(thianonyl)thiadiazole, (D) calcium salicylate, and (E) boron-containing succinimide. Lubricating oil compositions of Comparative Examples 1 and 2 are those which contain the (A), (B), (D) and (E) components, but does not contain the component (C).

Each of the above lubricating oil compositions was blended with a base oil (100 neutral oil having a viscosity at 100°C of 4.4 mm²/s), thereby obtaining lubricating oil compositions having the formulations shown in Table 1. The co-efficient of friction of each composition thus obtained was determined right after the composition was prepared, and after the composition was oxidised by being preserved at 130°C for 8 hours in the presence of nitrogen oxides gas. The results are shown in Table 1.

All of the lubricating oil compositions of Examples 1 to 10 according to the present invention have low co-efficients of friction and excellent frictional properties, and there is almost no change in the co-efficients of friction even after the compositions are heated at 130°C for 8 hours and oxidised. It is thus known that the lubricating oil compositions of the invention have excellent resistance to oxidation. In contrast to this, although the lubricating oil compositions of Comparative Examples 1 and 2, containing no sulfur compound, the component (C), have low co-efficients of friction right after the preparation thereof, they have increased co-efficients of friction after they are heated at 130°C for 8 hours and oxidised. It is thus known that the comparative lubricating oil compositions are poor in resistance to oxidation.

Effects of the invention

The lubricating oil compositions of the present invention are prepared by blending a base oil with an oxymolybdenum sulfide dithiocarbamate having a specific structure, a zinc dialkyl dithiophosphate, a sulfur compound, a metallic detergent and a boron-containing compound. Therefore, they not only have excellent anti-wear properties, but also exhibit high resistance to oxidation even at high temperatures in the presence of nitrogen oxides gas, thereby maintaining excellent frictional properties (friction-reducing properties) for a prolonged period of time. The lubricating oil compositions of the present invention are thus useful as lubricating oils for internal-combustion engines, automatic transmission gearboxes, dampers and power steering; they are particularly useful as lubricating oils for internal-combustion engines.

		EXAMPLE					
		1	2	3	4	5	6
Amount of molybdenum in C ₈ -MoDTC (ppm).		600	600	400		600	600
Amount of molybdenum in C ₁₃ -MoDTC (ppm).					600		
Amount of phosphorus in C ₈ -ZnDTP (primary) (wt. %).		0.10	0.10	0.10	0.10	0.06	0.1
Amount of sulfur in C ₅ -ZnDTC (wt. %).		0.15	0.05	0.10	0.10	0.10	
Amount of sulfur in C ₄ -CuDTC (wt. %).							0.05
Amount of sulfur in tetrabutylthiuram disulfide (wt. %).							
Amount of sulfur in dibenzyl sulfide (wt. %).							
Amount of sulfur in 2,5-di(4,5-dithianonyl) 1,3,4-thiadiazole (wt. %).							
Calcium salicylate (wt. %).		3.5	3.5	3.5	3.5	3.5	3.5
Amount of boron in boron-containing succinimide (wt. %).		0.03	0.03	0.03	0.03	0.03	0.03
Co-efficient of friction.	Right after preparation.	0.087	0.087	0.090	0.090	0.089	0.094
	After NOx-oxidation (130°C x 8 hours).	0.090	0.091	0.094	0.095	0.097	0.101

C₈-MoDTC : oxymolybdenum sulfide-N,N-dioctyl-dithiocarbamate.

C₁₃ MoDTC : oxymolybdenum sulfide-N,N-ditridecyl-dithiocarbamate.

C₈-ZnDTP(primary): zinc di-2-ethylhexylidithio-phosphate.

C₅-ZnDTC: zinc diamyl dithiocarbamate.

C₄-CuDTC: copper dibutyl dithiocarbamate.

	EXAMPLE					COMPARATIVE EXAMPLE	
	7	8	9	10	1	2	
Amount of molybdenum in C ₈ -MoDTC (ppm).	600	600	600	600	600		
Amount of molybdenum in C ₁₃ -MoDTC (ppm).						600	
Amount of phosphorus in C ₈ -ZnDTP (primary) (wt. %).	0.10	0.10	0.10	0.10	0.10	0.10	
Amount of sulfur in C ₅ -ZnDTC (wt. %).							
Amount of sulfur in C ₄ -CuDTC (wt. %).							
Amount of sulfur in tetrabutylthiuram disulfide (wt. %).	0.10						
Amount of sulfur in dibenzyl sulfide (wt. %).		0.10	0.05				
Amount of sulfur in 2,5-di(4,5-dithianonyl)1,3,4-thiadiazole (wt. %).				0.10			
Calcium salicylate (wt. %).	3.5	3.5	3.5	3.5	3.5	3.5	
Amount of boron in boron-containing succinimide (wt. %).	0.03	0.03	0.03	0.03	0.03	0.03	
Co-efficient of friction.	Right after preparation.					0.092	0.085
	After NOx-oxidation (130°C x 8 hours).					0.095	0.087
					0.090	0.086	
					0.096	0.167	
						0.175	

Claims

1. A lubricating oil composition characterized in that it is obtained by adding to a lubricating base oil (A) a sulfurized oxymolybdenum dithiocarbamate having an alkyl group with 8 - 18 carbon atoms. (B) a zinc dialkyl dithiophosphate having a primary alkyl group with 1 - 18 carbon atoms. (C) one or more kinds of sulfur compounds selected from the group consisting of zinc dialkyldithiocarbamates, copper dialkyldithiocarbamates, or nickel dialkyldithiocarbamates, each having an alkyl group with 2 - 18 carbon atoms, tetraalkylthiuram disulfides of which the carbon numbers of the alkyl group are 2 - 18, disulfides having an alkyl group with 2 - 18 carbon atoms, disulfides having an aryl group, an alkyl aryl group, or aryl alkyl group, with 6 - 18 carbon atoms, and thiadiazole compounds having a substituent with 3 - 24 carbon atoms and sulfur atom(s), sulfurized olefins, sulfurized fish oils, and sulfurized whale oils, (D) one or more kinds of metal-based detergents selected from the group consisting of calcium salicylates, magnesium salicylates, calcium sulfonates, magnesium sulfonates, and calcium phenates, and (E) a boron-containing compound, and in that based on the total amount of the composition the amount of the sulfurized oxymolybdenum dithiocarbamate-derived molybdenum is 200 - 2,000 ppm (weight ratio), the amount of the zinc dialkyl dithiophosphate-derived phosphorus is 0.02 - 0.15% by weight, the amount of the sulfur compound(s)-derived sulfur is 0.02 - 0.30 % by weight, the content of the metal-based detergent(s) is 1 - 10 % by weight, and the amount of the boron-containing compound-derived boron is 0.005 - 0.06 % by weight.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02436

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl⁶ C10M135/18, C10M139/00, C10M137/10, C10M135/20, C10M135/36, C10M151/02, C10M151/04, C10M159/20, C10M155/04, C10N10:12, C10N10:04, C10N10:02, C10N10:16, C10N30:06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) Int. Cl⁶ C10M135/18, C10M139/00, C10M137/10, C10M135/20, C10M135/36, C10M151/02, C10M151/04, C10M159/20, C10M155/04, C10N10:12, C10N10:04, C10N10:02, C10N10:16, C10N30:06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 62-181397, A (Amoko Corp.), August 8, 1987 (08. 08. 87) & US, 4767551, A & EP, 225580, A2	1
X	JP, 57-42797, A (Masaaki Takase), March 10, 1982 (10. 03. 82) (Family: none)	1
X	JP, 1-503545, A (Max Grill GmbH.), November 30, 1989 (30. 11. 89) & EP, 286140, A1	1
X	JP, 5-311188, A (Toyota Motor Corp.), November 22, 1993 (22. 11. 93) & US, 5389452, A & EP, 569006, A1	1
X	JP, 6-184578, A (Oronite Japan Ltd.), July 5, 1994 (05. 07. 94) (Family: none)	1

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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